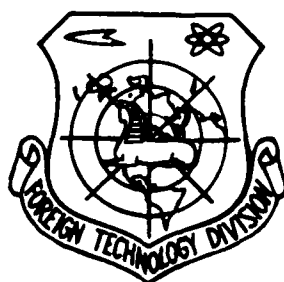AD-A225 345

FOREIGN TECHNOLOGY DIVISION

RESEARCH ON HIGH PERFORMANCE ORGANIC SILICON ABLATIVE MATERIALS FOR USE IN
SOLID ROCKET MOTORS

by

Sun Weijun

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TITLE :   RESEARCH ON HIGH PERFORMANCE ORGANIC SILICON ABLATIVE
MATERIALS FOR USE IN SOLID ROCKET MOTORS.

AUTHOR: SUN WEIJUN

[SUMMARY] This article discusses the effects of the structure of
organic silicon resins (R/Si and Me/Ph molecule chain forms and
comonomer structures) on the thermal stability of materials and
ablative properties. Opting for the use of special composite
techniques and precise formulation designs, it is possible to compound
resins with structures that are linear and branched. They have small
weight losses under heat. The char yield ratios are high. The
charring layers have great strength, and anti-scouring properties are
good. Utilizing endothermic chemical reactions that occur at high
temperatures between fillers in order to design materials for
formulation, it is possible to effectively lower the cold wall
temperature, improving ablative properties.

Key Terms: Organic Silicon Resin, Ablative Materials, Rocket
Motor, Coating

1. FORWARD

During the last twenty or thirty years, ablative materials in
resin composites, material formulation designs, property evaluation
and aspects of applications have acheived a clear series of steps
forward. However, in the matter of the ablative material high
performance properties to satisfy the high pressure (>9MPa) of solid
fuel rocket design, there still exists quite a distance to go. This
has primarily to do with deficiencies in the high temperature
resistance of materials and their high pressure gas flow scouring
properties. V.C. Lazarro discovered the use of oxide of boron
compounds to treat SiO_2 fibers. However, the materials manufactured
were only suitable for heat protection below $2000^\circ C$[1]. A.J.
Ramseyer chose to make use of carbon fibers and ceramic fillers or
packing materials in order to improve the scouring resistance
properties of organic silicon. This is nothing else than the Dow
Corning Company's DC93-104 product[2,3]. However, when the U.S.

Navy Weapons Center (NWC) uses it to make the insides of motor gas exhaust tubes, under pressures of 10.5 MPa, the ablation rate or ratio is higher than 0.9mm/s[4]. As far as the Soviet Union's V-58 organic silicon insulating coating is concerned, it is used in the inner linings of anti-tank rocket motors. Under pressures of 9~10 MPa, the ablative rate or ratio also reaches as high as 0.42mm/s and higher. Scouring is severe.

With the problems above in mind, we went through a precise design formulation of organic silicon resins. We selected appropriate and special composite techniques and synthesized scouring-resistant organic silicon resins with high strength charring layers and high char yield ratios or rates. Taking this as the basic material, we formulated appropriate filler materials, including filler materials capable of producing endothermic chemical reactions under high temperatures and produced high performance ablative materials.

2. TESTING

2.1 THE SYNTHESIS OF ORGANIC SILICON RESINS

The monomers used were CH_3SiCl_3, $(CH_3)_2SiCl_2$, $C_6H_5SiCl_3$ and $(C_6H_5)_2SiCl_2$. The degree of their purity was standardized by the use of chemical methods and gas phase chromatography methods.

Methods of Synthesis: Under low temperatures, organic phases (containing monomers and solvents) and aqueous phases (containing water, solvents and additives) were mixed together to carry out cohydrolytic reactions. After hydrolytic reactions, the resins are washed to pH=7.0~7.5. They come out of the solvents with reduced pressure steam. After that, under temperatures lower than $180^{\circ}C$, one carries out fusing and contracting reactions. For end point control, we selected for use viscosity methods and gelatinization time methods.

2.2 COMPOUNDING OF FUSION COATINGS

The principal filler materials that were used were Cr_2O_3, mica, FA-1 and FA-2. FA1 and FA2 are basically non-organic filler materials processed from the laboratory. The solvent is alcohol. The

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compounding ratios of the filler materials are 30~50% of the coatings. The various constituents described above and the resins are crushed to the required degree of fineness on a ball crusher.

2.3 EVALUATION METHODS

The general properties of the resins and coatings were measured in tests carried out according to standard methods.

Heat-weight analyses were carried out on an LCT-1 model heat scales (product of the Beijing Analytical Instrument Plant). Analyses of thermal differences, besides being done on the LCT-1, were carried out on partial samples with a CDR-1 model thermodynamic difference analyzer (product of the Shanghai Weighing Instrument Plant). The material involved in the comparisons was α $-Al_2O_3$. The speed at which temperatures went up was chosen, in all cases, to be $10^{\circ}C$/min.

Infrared analysis was carried out on IK-27 (product of the Daojin Company) and UK-20 (product of the Zeiss Company) intrared spectrophotometer instruments.

Static ablative experiments were carried out on an oxyacetylene flame ablative test device (OA model) of our own manufacture. The amounts of flow of specific heat were respectively controlled to be $175\pm5cal/cm^2$. s and $40cal/cm^2$. s.

We used static tests of solid rocket motors to measure the actual ablative rates or ratios and the cold wall temperatures. The propellant used was double base powder. Specific thrust was 210~220 S. The maximum operating pressures for the motors were, respectively, 9.0 MPa and 17.0 ± 1.0 MPa.

The methods used to solve for the thermodynamic parameters of heat breakdown reactions can be found by refering to refernce [5].

3. RESULTS AND DISCUSSION

(1) The thermal stability and ablative properties of high polymer ablative materials are primarily determined by the structures of resins in the composition of the materials. Filler materials are only capable of partially improving their properties.

Tables 3.1 and 3.2 present the experimental results for the thermal stability and ablative properties of 5 types of ablative organic silicon coatings. GT-401 and GT-402 are basically products of

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laboratory research. GR-2, SY-18, and SY-19 are commercial products. The filler materials selected for use with these five types of materials all have basic consituents which are white mica or Cr_2O_3. Their principal distinctions are that the formulation design parameters are different in the organic silicon resins and that the synthesizing techniques are different. In Table 3.1, R/Si shows a number for organic substitution radicals of silicon ions. The smaller

Tab.3.1 Data of thermal analysis for five ablative coatings

材料 \ 性能	极限失重 % [3]	500°C失重 % [4]	热分析峰 I 最高温度°C [6]	热分析峰 II 最高温度°C [8]	有机硅树脂的配方设计参数 [9]	
					R/Si	Me Ph
G T-401	12.0	4.6	无	591	—	—
G T 402	12.2	4.3	无	590	1.45	3.00
G R-2	17.0	7.3	437	600	1.36	1.85
S Y-18	19.8	14.0	385	626	1.64	5 25
S Y-19	23.5	13.0	无	597	—	-

Tab.3.2 Data of thermodegradation kinetic and ablation for five ablative coatings

材料 \ 测试项目 [2]	动力学参数 [3]		烧蚀率/mm·s⁻¹ [6]		
	反应级数 n [4]	表观活化能 kcal/mol [5]	O₂—C₂H₂ 40cal/cm²·s	O₂—C₂H₂ 170cal/cm²·s	(P$_{max}$ = 9.0～9 5MPa)
G T-401	3.36	64.12	0.157	0.30	0.22～0 28
G T-402	2.24	42.64	0.213	0.35	—
G R-2	1.36	20.46	0.224	—	—
S Y-18	1.24	36.98	—	—	0.33～0.38
S Y-19	0.81	17.50	—	—	0.44～0.47

KEY:

Tab. 3.1 (1) Material (2) Property (3) Weight Loss Limit (4) Weight Loss (5) Heat Decomposition Peak I (6) Maximum Temperature (7) Heat Decomposition Peak II (8) Maximum Temperature (9) Formulation Design Parameters of Organic Silicon Resins

Tab. 3.2. (1) Material (2) Measured Item (3) Thermodynamic Parameters (4) Reaction Series (5) Apparent Activation Energy (6) Ablative Rate

the value is, theoretically, the larger the degree of cross linking or coupling is. Me/Ph expresses the the value of the ratio between substitution phenyl radicals and substitution methyl radicals in the composition of the monomers of resins. The smaller the values are, the higher the amount of phenyl radicals contained. Because of this, it follows, for different values of R/Si and Me/Ph, that the chemical

compositions and degrees of theoretical cross linking or coupling for the corresponding resins are different. The synthesizing techniques are determined by the ratio and molecular weight of the interconnected, cyclical structures in the resins. The data in Table 3.1 and Table 3.2 clearly show that the striking differences in the stability and ablative properties of the five types of coatings are produced by differences in the resins used and in their structures (which will be discussed again later).

As far as the organic silicon resin used in GT-402 coating is concerned, due to the fact that we selected for use a special type of synthesizing technique, as a result, we basically eliminated the interconnected cyclic structures. Comparing it to the work in reference [6], it is possible to see that, in spite of the fact that the two of them use filler materials and organic resins whose chemical compositions are almost completely in line with each other, it is also true, however, that the organic silicon resin used in the latter contains considerable quantities of D_3 and D_4 structures. Because of this, the thermal stabilities differ greatly from each other. GT-402, at $500^{\circ}C$, had a weight loss which was only 4.3%. However, the latter still reached as high as 10-11% for a difference of over 100%.

As far as the two types of coatings, GT-401 and GT-402, are concerned, although the filler material structures are quite different, it is also true, however, that, due to the fact that we selected for use similar resin formulation design parameters and sysnthesis techniques, because of this, the thermal stabilities and ablative properties were relatively close. GT-401, in ablative properties, is superior to GT-402. The main thing is that, in the principal Si-O-Si chain, it introduced special phenyl radical monomers. It follows from this that the influence on ablative properties of the chemical structures of the comonomer chain sections of organic silicon resins are a main factor.

(2) The Effects of Synthesizing Techniques on Resin Structures and Properties.

In order to make the resins, after solidification, able to reach the designed degree of capablity, it is then necessary to set up methods, in the synthesis process, to avoid interconnected cyclical reactions. Interconnected cyclic reactions were not only lost and

used as coupling reaction activity centers (cinnamic alcohol radicals), lowering the coupling density. At the same time, this also led to a partial low polymer or low polymer substance production. Its result was to lower the thermal stability and ablative properties of the materials. The reason why organic silicon resins, under high temperatures, show thermal reversibility lies primarily in this.

With the interconnected cyclical structures in resins, it is possible to use infrared light spectra to make convenient measurements. Fig. 3.1 gives the infrared light spectra in the range of wave numbers $900\sim1300cm^{-1}$ for organic silicon resins produced under six types of different hydrolysis conditions. As far as the $1000\sim1200cm^{-1}$ interval of infrared absorption is concerned, it is possible to capture the structure of the $\equiv$ Si--O--Si $\equiv$ chain[7]. $1030cm^{-1}$ position absorption corresponds to the D_3 ring body (cyclic trisiliconoxyalkane). $1140cm^{-1}$ absorption corresponds to D_4 ring body (cyclic tetrasiliconoxyalkane). The sharp absorption peak between 1030 and $1140cm^{-1}$ corresponds to even larger silicon oxide chain ring body structures. From the Fig.'s it is possible to see that the organic silicon resins produced under hydrolysis conditions a,b,c, and d possess ring or cyclic body structures. However, organic silicon resins produced under hydrolysis conditions m and n possess linear structures. Due to the fact that functional energy is greater than 2, it follows that it is a branched linear type structure.

As far as the resins used in GT-401 and GT-402 are concerned, due to the fact that we, respectively, selected for use m and n hydrolysis conditions, it follows that they possess good thermal stability and ablative properties. Of course, the areas of difference between the synthesizing techniques still have an influence on the technical properties of the coatings and resins. Resins with linear forms and branched structures possess relatively high viscosities, relatively low temperatures of solidification, and excellent technical properties.

It follows from this that, as far as obtaining high performance ablative organic silicon resins is concerned, it is necessary to make the resins basically free of ring body structures, causing them to
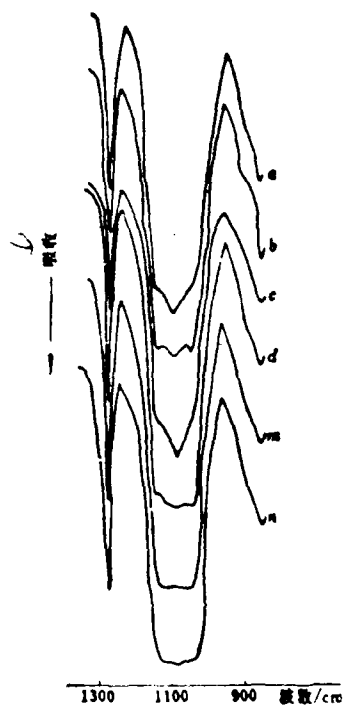
6

Fig 3.1 IR spectrum for silicone
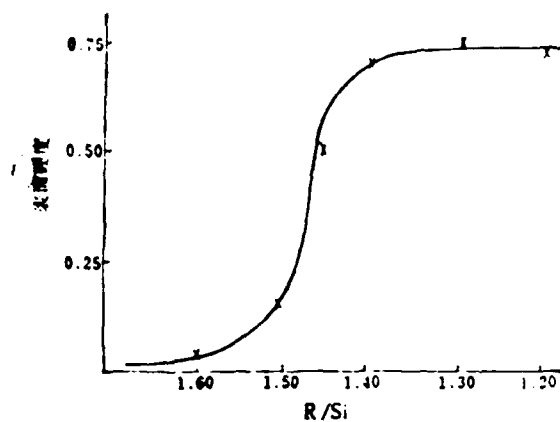resins made under various conditions
of hydrolysis

Fig. 3.2 R/Si—surface hardness relations

Fig. 3.1 (1) Absorption (2) Wave Number
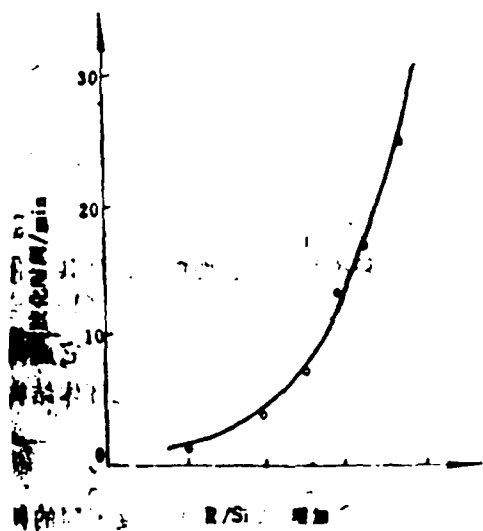Fig. 3.2 (1) Surface Hardness

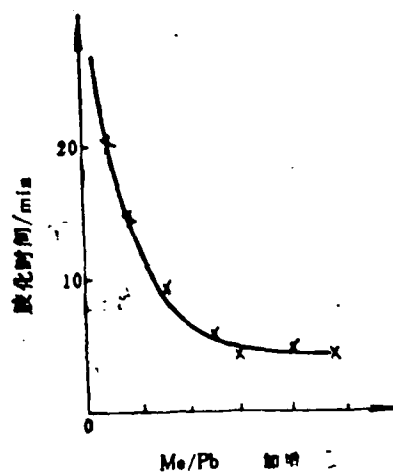Fig. 3.3 R/Si-gel time relations (schematic)

Fig. 3.4 Me/Pb-gel time relations (schematic)

Fig. 3.3 (1) Gelatinization Time (2) Increase
Fig. 3.4 (1) Gelatinization Time (2) Increase

turn into branched linear form structures. As far as synthesizing techniques are concerned, they must, in particular, be chosen appropriately under conditions with monomer co-hydrolysis. This is key to guaranteeing structures with no ring bodies.

(3) The Influence of the Formulation Design of Resins on Their Properties

Through fixing synthesizing techniques and varying resin functional energy design values (R/Si), it is possible to obtain a series of resins with different surface hardnesses. Their hardness distribution is from 0.07 to 0.73. The surface hardnesses of the coatings manufactured through their use are from 0.20-0.50. For the results, see Fig. 3.2. The degree of hardness is a macro physical quantity for the actual coupling density of the resins. A rise in it signifies a rise in the coupling density. As far as low resin hardness is concerned, that is, coatings manufactured with resins having low coupling densities, static motor tests were made, and the ablative coating layers were almost scoured clean. This corresponded to cold wall temperatures which reached 600°C and higher. However, in the case of resins with high hardnesses, that is, coating materials manufactured with resins having high coupling densities, the scouring resistance was excellent. The ablative coating layers (charring layers and breakdown layers, as well as original coating layers) were completely preserved.

In order to provide materials with the appropriate technical properties for construction work, the resins used should possess the corresponding coupling reaction activity. The influence of functional energy (R/Si) and the mutual correlation values (Me/Ph) between different organic silicon radical groups on resin gelatinization times are shown in Fig. 3.3 and 3.4.

Within the range of the experiments, following along with decreases in the functional energy design values, that is, increases in R/Si or increases in the amount of phenyl radicals contained, that is to say, reductions in Me/Ph, thermal weight losses of resins increase, thermal stabilities vary, and char yield rates are reduced. Although both the two design parameters described above have an influence, it is true, however, that, in a comparison, increases in

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functional energy design values are more effective in reducing thermal weight losses than increasing the specific values of methyl radicals and phenyl radicals.

It should be pointed out that, under conditions of a fixed functional energy design value, the design for Me/Ph values is also quite important. The existance of a certain amount of phenyl radicals, in talking about ablative organic silicon resins, is a necessity. In the thermal breakdown of resins, they must exist. Only then can there be the formation of charring. The importance of char yield or carbon formation is stressed in quite a number of references. However, too high an amount of contained phenyl radicals not only does not help improve the status of char yield, on the contrary, it lowers the materials' thermal stability and ablative properties. Because of this, in order to give attention to both char yield and thermal stability, improving the ablative properties of materials and precise design Me/Ph are important.

In various types of phenyl radical monomers, aiphenyl radical monomers take part in co-condensation reactions. This is advantageous to the improvement of ablative properties.

(4) Making use of the endothermic chemical reactions that take place at high temperatures between filler materials to design the formulation of ablative materials is very effective in raising ablative insulating properties and lowering cold wall temperatures.

Experimentation clearly demonstrates that, when both the FA-1 and FA-2 types of filler materials exist at the same time in the formulation of coating materials (filler materials also include Cr_2O_3 and white mica), going through thermal differential analysis demonstrates clearly that, at 950~1000°C, there occured a relatively large endothermic chemical reaction. When the various filler materials were compounded independently to carry out the tests, at the times when FA-2 was not contained, no endothermic peak occured. We recognize that it is FA-2 and Cr_2O_3, at high temperatures, which give rise to endothermic oxydation reduction reactions. Selecting for use this type of formulation, we carried out static rocket motor

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tests. The maximum cold wall temperature can be lowered approximately 200°C. Of course, this cannot help but be a contribution, after determining resin and material scouring resistance, to the insulating efficiency of the endothermic reactions which manifest themselves and are carried out between filler materials.

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